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Oxidation of Sulphur Dioxide using Micro- and Nanoparticles of various Iron Oxides

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Abstract: Sulphuric acid is the chemical with highest production rates in the world. At present, it is mainly synthesized using vanadium pentoxide as catalyst, which determines the applied production process particularly in terms of gas pre-treatment and heat management. For processes, which cannot be run with vanadium pentoxide, alternative catalysts are required to make different SO₂ qualities accessible to sulphuric acid production. Ferric oxides are a very promising alternative, since they combine higher thermal with improved chemical stability. Within this study, various ferric oxides were examined with regard to conversion rates and structural changes during application. Effects of crystal structure, particle size as well as thermal treatment and the influence of precipitation conditions were studied. Although conversion rates are very promising, it has become apparent, though, that these materials cannot compete with vanadium pentoxide in terms of conversion rate as well as long-time stability, yet. Nevertheless, from the results of this study, it is clear that high potential lies in focused catalyst optimisation.

Introduction

The oxidation of sulphur dioxide to sulphur trioxide is one of the most often applied catalytic processes, since it is the key step for sulphuric acid production. Sulphuric acid is the most important chemical in the world as well as the one with the highest production rate. The global sulphuric acid market size reached a volume of 284.4 million metric tons in 2020 and is likely to reach a volume of 311 million metric tons by 2026.^[1] As a base chemical it finds manifold applications, spanning from metallurgic processes to chemical syntheses.^[2–4]

At present, the contact and double contact processes using vanadium pentoxide catalysts are widely used for sulphur dioxide oxidation. The applied process is chosen in dependence on the sulphur dioxide source used and its characteristic properties in

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concentration.^[3,5] Thus, sulphur dioxide containing gases with constant or temporal fluctuating sulphur dioxide concentrations in the range of 2-12 vol.% can be converted with these processes.^[2,3,5–7] Higher concentrated gases need to be diluted or incompletely converted for the purpose of limiting adiabatic temperature increase in the course of the reaction, since the maximum temperature is determined by the catalyst.^[6,8-10] In contrast to that, application of lower sulphur dioxide concentrations requires additional heating, as heat production during reaction is insufficient for autothermal operation.^[3] Furthermore, utilisation of sulphur dioxide containing exhaust gases necessitates the implementation of additional process steps prior to conversion for separating water, catalyst poisons, such as fluorine or chlorine, as well as arsenic, which affects recycling.^[3-5] Altogether, execution of contact processes is essentially determined by operating temperature range and chemical properties of the vanadium pentoxide catalyst.^[2-8,11,12,13] as well as the need for recycling of spent catalyst, since it is toxic ^[4,14], and a complete recycling is mandatory ^[4,5].

terms of temporal fluctuations as well as sulphur dioxide

As the use of exhaust gases for sulphuric acid production becomes more and more important, research on alternative catalysts has been intensified in recent years.^[6–9,13–21] Promising materials should combine a wider operating temperature range with improved stability against poisoning. Thus higher concentrated gases typical for modern metallurgic processes applying oxygen could be used directly ^[6], while other exhaust gases could be applied in a process with an improved number of process steps.

Ferric oxides are very promising materials, since their catalytic activity for sulphur dioxide oxidation is sufficient for applications in industrial processes and its durability against poisoning is known for decades.^[3,5,12,16] Additionally, they possess a higher thermal stability in comparison to vanadium pentoxide based catalysts, which enables their application up to 800 °C.^[6,15,17,18] However, maximum conversion is achieved at temperatures in the range of 550 – 760 °C and often without reaching thermodynamic equilibrium.^[6,8,14,22,23] Thus conversion rarely reaches levels achieved with vanadium pentoxide and patented processes mostly combine catalyst layers of vanadium pentoxide and ferric oxide.^[8,9,15]

However, recent research has shown that catalytic activity as well as onset temperature of SO₂ oxidation of ferric oxides can be improved by reducing the particle size, although only gases with sulphur dioxide concentrations in the ppm-range where examined.^[14] Additionally, investigations on the application of sulphated ferric oxides showed that these materials possess improved catalytic activity in acid-base catalysis.^[24] Moreover, the incorporation of sulphate into the catalyst precursor is promising, since sulphate coordinated by the ferric oxide lattice can be seen as preformed catalytic active site for sulphur dioxide coordination.

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Therefore, this study deals with the application of sulphated ferric oxides for sulphur dioxide oxidation, which is a continuation of former investigations concerning reproducible production of sulphated ferric oxides using a microjet mixer ^[25] and research on the influence of precipitation parameters ^[25] as well as calcination temperature ^[26] on chemical and structural properties. However, for better classification of observed effects and dependencies as well as identification of influencing parameters, various commercially available ferric oxide micro- and nanoparticles (pigments, ferric oxide nanoparticles and microparticles synthesized for research application) were examined, too.

Results and Discussion

General trends

Former investigations on the reaction of ferric oxides with sulphur dioxide covered a wide temperature ^[14,27,28] as well as a wide concentration range ^[8,14,18,23,29], and results differed largely. Therefore, experiments with ferric oxide microparticles were done first for the purpose of identifying promising reaction conditions as well as general trends in physical and chemical changes of the used catalyst during the catalytic reaction. The investigated parameters comprised temperatures from 450 to 650 °C and sulphur dioxide concentrations in the range of 5.0 - 28.5 vol.%. These ranges were chosen, since they cover conditions applied for catalysis with vanadium pentoxide enabling comparison of the results as well as conditions relevant in exhaust gas treatment. The value of 28.5 vol.% SO₂ resulted from stoichiometric values of sulphur dioxide and oxygen concentration in the reactant gas streatment.

From Figure 1 can be seen, that within the temperature range up to 600 °C conversion increased continuously. This dependency was observed before and is caused by temperature dependent kinetics.^[14] However, with further ascending temperature, concentration dependent behaviour was found to result in a maximum conversion between 600 and 650 °C. Thus, the highest conversion rate was found at a lower reaction temperature, when the reactant concentration was increased. In fact, only experiments with 5 vol.% SO2 gave the thermodynamically limited within the examined temperature range, vield while thermodynamic equilibrium is expected to be reached below 750 °C for the application of 10 and 15 vol.% SO2. As the thermodynamic equilibrium lies rather on the reactant side in this temperature range, resulting possible conversion rates are lower than yields reached at 650 °C. Finally, experiments with 20 and 28.5 vol.% SO₂ were characterised by a decreased conversion at 650 °C, without reaching thermodynamic equilibrium conversion at all. This is in agreement with preceding studies showing both results: experiments with conversion levels always below thermodynamic equilibrium ^[22,23] as well as studies in which the thermodynamic equilibrium was reached [6,14,22]. Interestingly, investigations on Pt/Pd catalysts for sulphur dioxide oxidation examined by Koutsopoulos et al. [19,20] also showed maximum conversion degrees without reaching thermodynamic equilibrium. What they concluded was that the position of observed maximum conversion depended on reaction conditions including volume

flow rate and catalyst loading. Thus, investigations on various catalyst loadings were done in this study resulting in space velocities in the range of 350 to 750 h⁻¹ applying 10 vol.% SO₂ at 650 °C. However, these experiments did not show any significant effects on conversion, which is the reason why these parameters were not varied in consecutive experiments.



Figure 1. Dependence of thermodynamically (dashed line) and experimentally determined (solid line) sulphur dioxide conversion rates from temperature and sulphur dioxide concentration.

A comparison of conversion rates determined in this work with those from earlier studies (Table 1) showed that they differ to a large extent due to different composition and production processes. Hematite microparticles studied in this work showed intermediate catalytic activity.

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lable	1. Com	parison o	t conversion	rates with	literature	reports

Catalyst	c(SO ₂)/	Τ/	Conversio	Ref.
	vol.%	°C	n rate/ %	
α-Fe ₂ O ₃	5	450	22.5 ± 2.5	This work
α-Fe ₂ O ₃	10	450	14.2 ± 0.8	This work
α-Fe ₂ O ₃	7.4	450	5 - 7	[16]
Sn _{25,9} Fe _{74,1} O _x	7.4	450	18	[16]
Catalyst synthesized from	7	640	56	[7]
dust containing Fe, Cu, Si,				
Zn, Pb				
Fe ₂ O ₃ supported on SiO ₂	20	600	72	[15]
Iron silicate	20	600	77	[15]
α-Fe ₂ O ₃	20	600	46.2 ± 3.9	This work

These differences are a result of varying synthesis methods as well as reactant gas and catalyst compositions. Additionally, catalytic conversion achieved with ferric oxide is lower than that of vanadium pentoxide, which is known to reach thermodynamic equilibrium conversion, as long as sulphur dioxide concentration is between 2 - 12 vol.%.

In order to investigate the effect of sulphur dioxide oxidation on the catalyst, the ferric oxides used were analysed before and after the reaction for their specific surface area as well as their chemical composition. In general, XRD analyses showed that

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after conversion the catalysts were composed of hematite, α -Fe₂O₃, and ferric sulphate, Fe₂(SO₄)₃ (Figure S1 and S2).

However, the quantity of sulphate incorporated into the catalyst materials was never the same as under reaction conditions, since ferric sulphate was partially decomposed to ferric oxide and sulphur trioxide during cooling down as a result of changing gas atmosphere at elevated temperature. But as all experiments were conducted following the same cooling procedure, a comparison of the materials treated at the same reaction temperature is feasible, and some conclusions on experiments at differing temperatures can be drawn as well. Results of these analyses are outlined in Figure 2 and Figure 3.



Figure 2. Temperature dependent sulphation grade of ferric oxide microparticles in dependence on used sulphur dioxide concentration.

As can be seen in Figure 2, the ferric sulphate ratio in treated ferric oxide catalysts depended strongly on temperature as well as sulphur dioxide concentration. Iron oxides can interact with sulphur dioxide in many ways. Thus, both adsorption and direct catalytic conversion of SO2 are possible. Which mechanism dominates depends strongly on the reaction temperature. The adsorption of SO₂ with the formation of iron sulphate (equation 1) occurs mainly below the decomposition temperature of iron sulphate (equation 2, T>600 °C; see Figure S3), while the direct catalytic conversion predominates at higher temperatures and iron sulphate can no longer be detected at envious SO2 concentrations. With increasing temperature sulphation increased until a maximum was reached between 500 and 600 °C. This maximum depended on reactant concentration and was reached at higher temperatures with increasing sulphur dioxide concentration. Expectedly, ferric sulphate ratio increased at higher sulphur dioxide concentration. These observations are a result of the chemical reactions involved:

$$\begin{array}{rcl} Fe_2O_3 + 1.5 \ O_2 + 3 \ SO_2 \ \rightleftharpoons \ Fe_2(SO_4)_3 & (1) \\ Fe_2(SO_4)_3 \ \rightleftharpoons \ Fe_2O_3 + 3 \ SO_3 & (2) \end{array}$$

Resulting in the over-all chemical equation

$$SO_2 + 0.5 O_2 \rightleftharpoons SO_3$$
 (3)

The formation of ferric sulphate is a function of sulphur dioxide concentration and temperature dependent positions of reaction equilibria. In addition, an increasing degree of sulphation with increasing temperature is a result of improved kinetics of reaction (1), until above 500 °C both ferric sulphate decomposition (see Figure S4) (2) and the reverse reaction of (1) gain in importance, which in turn cause the degree of sulphation to decline. These effects are superimposed by the desulphation during cooling, which is more pronounced if the reaction was carried out at higher temperatures, which favours the decomposition of iron sulphate and leads to a higher reaction velocity. Thus, catalysts treated at 650 °C with sulphur dioxide concentrations in the range of 5 to 10 vol.% did not contain any sulphate after cooling, although intermediary formation of ferric sulphate is essential for catalysis. However, sulphate was determined in materials treated at higher concentrations. This is a result of reactions (1) and (2): With increasing sulphur dioxide concentration in the reactant gas the sulphation ratio of the ferric oxide catalyst during the catalytic reaction grows, too. As all materials were cooled down in the same manner, the reaction velocity of ferric sulphate decomposition (2) is independent from ferric sulphate ratio. At high sulphation ratios, reaction velocity is not high enough for complete decomposition of ferric sulphate during cooling down, which is why sulphate can be detected in these used materials.



Figure 3. Dependence of specific surface area of ferric oxide microparticles on temperature and treatment with sulphur dioxide.

Based on these conclusions the relationship between reaction conditions and observed specific surface area was examined (Figure S6-S10). As shown in Figure 3, specific surface area decreased continuously with increasing temperature in the absence of sulphur dioxide, which is an outcome of thermally induced sintering. Characterisation of catalyst materials collected after catalytic conversion of sulphur dioxide did not give a clear indication, though, but comparison of sulphation with measured specific surface area visualized in Figure 4 shows that there is a connection between both parameters, as an increasing specific surface area is linked to decreasing sulphation. This relationship becomes clear, when it is considered that reaction (1) occurs at first with highly energetic ferric ions of the crystalline lattice. These ions are characterised by low coordination and are mainly situated

at corners and edges.^[30] In the course of sulphation these crystalline imperfections are smoothened and pores are filled with formed ferric sulphate, which causes the observed decrease in surface area.



Figure 4. Connection between measured specific surface area and ferric sulphate ratio of used ferric oxide materials.

As a consequence of the significant changes in specific surface area S_{Kat} during reaction, the effective reaction velocity r_{eff} , which is dependent from specific surface area, is defined according to equation (4) including conversion rate U_{SO_2} , initial sulphur dioxide concentration c_{0,SO_2} , volume flow rate V and the mass of applied catalyst m_{Kat} :

$$r_{eff} = \frac{U_{SO_2} \cdot c_{0,SO_2} \cdot \dot{v}}{m_{Kat} \cdot S_{Kat}}$$
(4)

Using this equation, the interplay between effective reaction velocity, conversion as well as reaction temperature and reactant concentration is graphically represented in Figure 5 and Figure 6. It shows that the effective reaction velocity depended on temperature as well as sulphur dioxide concentration, whereby the effect of reactant concentration was most pronounced at 600 °C. The increased sulphur dioxide partial pressure, on the one hand, promotes the decomposition of iron sulphate to set the thermodynamic equilibrium (equation 3) and, on the other hand, increases the formation of iron sulphate according to equation 1. Up to 600 °C reaction rates were found to increase, which is mainly owed to decreasing effects of kinetic hindrance. Lower reaction rates found at 650 °C are a consequence of a declining conversion with increasing temperature as the thermodynamic equilibrium of sulphur dioxide oxidation (3) is shifted to favour the decomposition of sulphur trioxide. In fact, this decrease in effective reaction velocity was more pronounced than the observed decrease in conversion rate as specific surface area increased from 600 to 650 °C due to reduced sulphation of the spent catalyst.

Considering these analyses, the results shown in Figure 1 can be interpreted in a way that decreasing conversion with increasing sulphur dioxide concentration at low temperatures is owed to a higher degree of catalyst sulphation. Since sulphation causes catalytically active sites blocked, it is the interaction of reaction (1) and (2), which determine catalytic activity with increasing temperature. It is apparent that experimentally determined conversion rates at 550 °C and 5 vol.% SO₂ were very similar to those at 600 °C and 10 vol.% SO₂, although effective reaction rates varied significantly. As can also be seen from Figure 1, conversion decreased less pronounced for 20 and 28.5 vol.% SO₂

at 650 °C compared to what had been expected from the changes in sulphur dioxide oxidation equilibrium.

The reason is a higher reaction velocity of ferric sulphate decomposition marked by decreasing ferric sulphate ratios measured after application when going from 600 to 650 °C. For example, the ferric sulphate ratio of ferric oxide treated with 20 vol.% SO₂ decreased from 40.65 ± 3.91 % to 8.52 ± 3.34 % in this temperature range. As stated before, this observation was accompanied by an increase of specific surface area from 2.14 ± 0.07 to 3.62 ± 0.16 m²/g, causing the over-all effective reaction velocity to decrease from 2.05 ± 0.24 to 1.11 ± 0.08 µmol/m²s.







Figure 6. Dependence of effective reaction velocity of ferric oxide microparticles on applied temperature and sulphur dioxide concentration.

Based on these results further investigations were done using 10 vol.% SO₂ at 600 °C. These reaction conditions bear the potential for identification of materials with better catalytic properties and maximum conversion rates within the range of conditions applied for catalytic conversion with vanadium pentoxide (V₂O₅).

Application of precipitated ferric oxides

Former studies had shown that chemical as well as physical properties of ferric oxides were strongly effected by precipitation conditions and subsequent treatment.^[25,26] These variations were studied for a potential impact on catalytic activity in sulphur dioxide oxidation. For the purpose of verifying such dependences, experiments with ferric oxides synthesized in our laboratory were conducted. In the following, influences of thermal treatment, mixing conditions during precipitation and aging were investigated. Finally, the choice of applied reaction temperature was checked and the material showing highest conversion was used for several successive experiments.

Influence of annealing temperature

From our former study concerning precipitation of ferric sulphate with ammonia solution it was known that 2-line-ferrihydrite and schwertmannite were formed as a function of pH during precipitation.^[25] Samples of both materials were annealed at 300. 500 and 900 °C for 8 h in a subsequent study.^[26] These samples were chosen for investigation of catalytic activity, too. However, materials treated at 300 and 500 °C are likely to undergo physicochemical alterations during heating-up to the reaction temperature of 600 °C. This expectation was evidenced by analyses of specific surface areas of annealed ferrihydrites showing a significant decrease of specific surface area between $(52.6 \pm 0.6 \text{ m}^2/\text{g})$ and $600 \degree \text{C}$ $(29.5 \pm 0.4 \text{ m}^2/\text{g}).$ 500 Considering this fact, it was expected that the catalytic activity does not differ significantly for these materials, while ferric oxides treated at 900 °C should show noticeable differences. Figure 7 displays the results of catalytic oxidation revealing that these expectations were right. They clearly confirm that sintering during annealing at temperatures above 800 °C affected catalytic activity.^[27,31] Interestingly, obtained conversion rates depended on the used precursor, which is very important for catalyst development. Thus, catalytic activity of treated schwertmannite was higher than that of formerly tested microparticles (section 3.1) as well as ferrihydrite.



Figure 7. Dependence of sulphur dioxide conversion on annealing temperature; reaction temperature: 600 °C, feed gas composition: 10 vol.% SO₂, 18 vol.% O₂ and 72 vol.% N₂.

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In order to find an explanation for these results, analyses concerning chemical and physical properties were done. They showed that under reaction conditions any tested material was converted into hematite and ferric sulphate. A deviating catalytic activity is therefore not necessarily influenced by the particle crystallinity. However, analyses of ferric sulphate ratio, specific surface area and diameter of formed hematite crystallites showed some differences. As summarized in Table 2, analyses of materials treated at 300 and 500 °C were found to have very similar specific surface areas and hematite crystallite diameters after the catalytic reaction, while the degree of sulphation depended on the applied precursor. The decrease of specific surface area was a characteristic property of each individual iron oxide, a detailed study of which had been reported before.^[6] In general, the catalytic conversion reaction caused an increase of sulphation and crystallisation, whereas specific surface area decreased. Upon comparing the materials annealed at 900 °C it became evident that during this pre-treatment ferric oxides were formed, the properties of which were not significantly affected by the catalytic reaction. This is in agreement with former studies ^[27,31] and a result of high annealing temperature which causes the development of ferric oxides with very low specific energy. Hence, resulting catalytic activity is much lower than that of ferric oxides treated at lower temperatures. Remarkably, catalytic conversion still depended on the used precursor, which was in connection with differing specific surface areas and structures. This shows that differences in particle structure observed before [26] had an influence on the catalytic conversion and achievable product yields, even after treatment at 900 °C.

Table 2. Analyses of fresh and spent ferric oxide

	Annealing temperature	Ferric sulphate ratio/ wt.%		Specific surface area/ m ² /g		Hematite crystallite diameter/	
	/ °C	Fresh	Used	Fresh	Used	Fresh	L'sed
2-	300	3.5 ± 0.3	49.6	155 ± 2	1.7 ±	14 ± 2	37 5
Line-			± 0.7		0.1		
ferri	500	3.3 ± 0.2	49.3	53 ± 1	1.2 ±	37 ± 9	?9 ± 17
hydri			± 0.9		0.1		
te	900	0 ± 0.1	0 ±	<1	<1	96 ± 1	(0±1)
			0.1				
Sch	300	28.0 ± 1.0	57.2	26 ± 1	1.3 ±	-	· 5: 22
wert-			± 0.4		0.1		U
man	500	28.7 ± 1.4	58.3	20 ± 1	1.4 ±	18 ± 7	7 9 ± 1ς
nite			± 0.9		0.1		
	900	0 ± 0.1	0 ±	2.2 ±	2.4 ±	96 ± 1	{∠±5
			0.1	0.2	0.2		

Influence of precipitation conditions

According to the results of the former section, the influence of precipitation conditions on the catalytic activity of ferrihydrites was investigated using materials annealed at 500 °C. For these purposes, samples were selected whose precipitation conditions differed with respect to ageing before separation from the liquid medium, reactant concentration, reaction temperature, mixing rate, application of aged ferrous sulphate solution and mixing regime. Experimentally observed conversion rates of all materials

separated directly after precipitation were in the same range of 35 ± 4 to 42 ± 4 %. However, ferrihydrite aged for one week in its mother liquor was more active (55 ± 3 %). This is due to changes in the crystalline structure of the precipitated ferrihydrite within this period resulting in an improved stability of the specific surface area during the catalytic reaction. Experiments with schwertmannite revealed the same relationship.

Influence of reaction temperature

After demonstrating that schwertmannite annealed at 500 °C was catalytically more active than ferric oxide microparticles and ferrihydrite at 600 °C it was important to find out whether this observation was correct for the entire temperature range of 450 - 650 °C. Thus, additional experiments with 10 vol.% SO2 were conducted. The results shown in Figure 8 proved that the choice of 600 °C was right, since this was the only temperature, where significant differences in catalytic activity were observed. Additionally, experiments at this temperature were characterised by highest differences of almost a factor of four in effective reaction velocity, which were due to the low specific surface area of treated schwertmannite and improved conversion. Decreasing reaction velocity of schwertmannite with further increasing reaction temperature was the result of an increasing specific surface area from 1.4 ± 0.1 to $16 \pm 1 \text{ m}^2/\text{g}$ since ferric sulphate decomposition occurred at high rates. Hence ferric sulphate ratio measured after the catalytic conversion decreased from 58 ± 1 to 11 ± 7 % while crystallinity of formed hematite increased. Since no significant temperature dependent changes in catalyst composition and specific surface area were noted at temperatures up to 600 °C, lower reaction rates observed in this range are a consequence of decreased conversion and kinetic effects. Thus, the deviating conversion rates detected at 600 °C were a result of kinetic effects as well as relative proportions of occurring reactions (1) and (2). This is evidenced by measured sulphation ratios of treated catalysts, which showed that sulphation of ferric oxide decreased already at 600 °C while sulphation of schwertmannite was stabile up to 600 °C and only decreased at even higher temperatures. These deviations in reaction behaviour are probably caused by precursor dependent differing catalytic active site structures.

Reuse of schwertmannite

When aiming at substituting vanadium pentoxide in industrial sulphuric acid plants besides catalytic activity also long-term stability is an important criterion. Former investigations by *Wingen et al.* ^[6] had proven that ferric oxides deposited on a catalyst support meet this requirement. Prior to long-term studies, though, this study focused on the behaviour of nanostructured ferric oxide synthesized in microjet mixers ^[25,26] with the objective of identifying influencing parameters on catalytic activity, before catalysts based on supported nanostructured ferric oxides are developed. These latter in turn will be investigated in a follow-up study in long-term experiments. Therefore, in order to simulate the effects taking impact on catalyst lifetime aged schwertmannite (annealed at 500 °C) was subjected to multiple short-term experiments, since repeated heating and cooling down is known to stress catalyst materials.



Figure 8. Dependence of conversion (solid line) and effective reaction velocity (dotted line) on applied ferric oxide; feed gas composition: 10 vol.% SO_2 , 18 vol.% O_2 and 72 vol.% N_2 .

Figure 9 illustrates, how conversion rates decreased from experiment to experiment. It was found, too, that conversion rates decreased less with each experiment, but no steady state was observed. This progress differed from the study by *Wingen et al.* ^[6] who described catalytic conversion to pronouncedly decrease from first to second usage, while further application of their supported catalyst caused only minor changes. However, in accordance to this report, increasing sulphation during multiple application was observed. The different behaviour is attributed to the application of a volume catalyst, the progressing deactivation of which is majorly results from blocking catalytically active sites by sulphation. Interestingly, specific surface area of spent schwertmannite decreased already within the first application to a value, which remained constant throughout the following experiments.



Figure 9. Effective reaction velocity, conversion and ferric sulphate ratio of multiple application of schwertmannite; reaction temperature: 600 °C, feed gas composition: 10 vol.% SO₂, 18 vol.% O₂ and 72 vol.% N₂.

Application of commercially available ferric oxides nanoparticles

For a better classification of the obtained conversion rates with ferrihydrite and schwertmannite, commercially available products were tested. For these purposes, pigments and ferric oxide nanoparticles synthesized for research applications were examined. The experiments showed additional parameters taking effect on the catalytic activity of ferric oxides.

Catalytic activity of commercially available ferric oxide products

Investigations on catalytic activity of pigments and ferric oxide nanoparticles were done with nine different samples. Conversion rates and effective reaction rates achieved with these materials are shown together with the best results of the former sections in Figure 10. Characteristic properties of the applied pigments are summarised in Table 3.

Table 3. Crystal phase (XRD) and physical properties of applied ferric oxide pigments

Pigment	crystal phase	Primary particle size [nm]	Particle shape
Bayferrox 110	Hematite	90	spherical
Bayferrox 180	Hematite	700	spherical
Bayferrox 415	Goethite	200 x 300	prismatic
Bayoxide E III	Hematite	200	spherical
Bayoxide E 8611	Magnetite	500	spherical
Bayoxide E F 20	Goethite	100 x 600	acicular



Figure 10. Effective reaction velocity and conversion rates of various ferric oxides at 600 °C. The dotted line marks thermodynamic equilibrium conversion as achievable with vanadium pentoxide; feed gas composition: 10 vol.% SO₂, 18 vol.% O₂ and 72 vol.% N₂

As shown in Figure 10, conversion rates in the range of 20 to 70 % were obtained with ferric oxides without optimisation. These results have to be assessed in view of the thermodynamic equilibrium (reached by V_2O_5) according to which conversion cannot exceed 79 %.

Thus, ferric oxides appear highly promising for the catalytic conversion. It has to be noted, though, that typical conversion rates ranged between 30 - 50 %. Therefore, ferrihydrite

possessed an average catalytic activity, while performance of schwertmannite was above-average. However, the highest sulphur trioxide yield obtained within this study was reached with goethite Bayoxide E F 20 (SO₂ conversion: 72,5%).



Figure 11. SEM analyses of ferric oxides after sulphur dioxide conversion at magnification 20,000 x. a) Bayferrox 110 (hematite); b) Bayferrox 415 (goethite); c) Bayoxide E 8611 (magnetite); d) Bayoxide E F 20 (goethite).

It is known from literature reports that a correlation exists between conversion rate and the crystal structure of the precursor.^[32] Expectedly the same applied to the catalyst materials investigated in this study. What was striking however was the finding that all tested materials were converted into hematite and ferric sulphate under process conditions. In other words, initial crystal phase affects the reaction outcome, although the catalyst material itself is converted into hematite during application. Additionally, SEM analyses (Figure 11) of four samples of various initial crystal structure showed that particle shapes differed largely after application. Thus, differing ratios of exposed crystal surfaces are likely to influence the experimentally observed catalytic conversion rates.

After all, the catalytic power of the investigated ferric oxides can be ordered as:

goethite > maghemite, schwertmannite > 2-line-ferrihydrite, hematite, magnetite

At this point however, there emerged a discrepancy between the findings of *Fu et al.* ^[33] and *Zhang et al.* ^[34], who identified opposing results concerning catalytic activity of hematite and goethite. Catalytic activities of the oxides give no homogeneous picture so far. This situation gives reason to assume that it may be crystalline defects, the role of which has to be considered thoroughly in order to explain the results satisfactorily. This issue will be matter of forthcoming investigations.

Additionally, particle size influences surface structure as well as catalytic conversion.^[30,35] Experiments with hematite were characterised by decreasing conversion with increasing particle diameter. Accordingly, experiments with hematite, 100 nm (IoLiTec) and Bayferrox 110 (90 - 100 nm) yielded comparable conversion rates of 45.9 ± 4.6 and 46.2 ± 1.7 %, while Bayoxide

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E III (200 nm) gave only 37.2 ± 2.0 %. This behaviour was already known before for the oxidation of sulphur dioxide ^[14,31], carbon monoxide and alcohols ^[36]. It was explained by an increasing number of catalytically active surface sites with decreasing particle diameter the structure of which is similar to the maghemite crystal lattice.^[30,35] In fact, maghemite was more active than hematite within this study.

In contrast to hematite, conversion increased from 37.9 ± 6.0 to 66.3 ± 2.9 % when maghemite with a particle size of 20 - 40 nm was used instead of a smaller fraction (7 - 10 nm). As SEM analyses (Figure 12) of maghemite samples after transformation into hematite showed that smaller maghemite particles gave larger hematite particles, this experimental result confirms the formerly stated relationship, too. This particular transformation behaviour was noticed before by *Feitknecht and Mannweiler* ^[37]. They concluded from microscopic analyses that during transformation of maghemite (15 nm) up to 100 primary particles stuck together to form an only hematite particle while bigger particles were transformed one by one.



Figure 12. SEM analyses of maghemite annealed at 600 °C (magnification 100,000). a) 7 - 10 nm, b) 20 - 40 nm.

Subsequent to sulphur dioxide oxidation, spent catalyst materials were analysed for their degree of sulphation as well as changes in specific surfaces, in order to retrieve further information on the observed trends.



Figure 13. Analyses of specific surface area of fresh and spent ferric oxide catalysts; reaction temperature: 600 °C, feed gas composition: 10 vol.% SO₂, 18 vol.% O₂ and 72 vol.% N₂.

As shown in Figure 13 surfaces of nanoparticles underwent the strongest decline, while this effect was less pronounced with all ferric oxide pigments. Decreasing surface stability with increasing specific surface area was caused by ascending potential energy favouring crystallisation and sintering. However, it emerged, too, that from surface area as well as surface stability one cannot conclude on the outcome of the catalytic conversion. For instance, Bayferrox 180 displayed a very stable surface area, but poor conversion, while Bayferrox 110 got a high specific surface area after use, but sulphur dioxide conversion was intermediate.

Measuring the degree of ferric oxide sulphation (Figure 14) confirmed that the applied materials did not contain any sulphate. Additionally, comparison with conversion rates of Figure 10 demonstrate that if there was no sulphate detectable in the spent catalyst this material was characterised by a low catalytic activity (e. g. Bayferrox 180), too. However, detection of sulphate was not a measure for the catalytic activity since Bayoxide E F 20 and hematite, 100 nm were characterised by comparable sulphation but circa 20 % differing conversion.



Figure 14. Analyses of ferric sulphate ratios of fresh and spent ferric oxide catalysts; reaction temperature: 600 °C, feed gas composition: 10 vol.% SO_2 , 18 vol.% O_2 and 72 vol.% N_2 .

Reuse of goethite Bayoxide E F 20

Best conversion rates within this study were achieved with Bayoxide E F 20 (72.5 %; V_2O_5 : 79 %), which was the reason why this material was investigated for repeated use. It was expected that this catalyst should be characterised by a rather low decrease in conversion rate from experiment to experiment since its surface structure was found more stable than this of schwertmannite. In fact, this assumption held true (Figure 15). Even after five experiments, conversion exceeded 65 % and the loss in activity was very low, while effective reaction velocity increased. However, the specific surface area declined continuously from the first application, while the degree of sulphation increased. Thus, specific surface area did not reach a minimum within the first application as found for schwertmannite. This indicates that smaller changes during the first application are not due to a higher stability but slower progress of surface reorganisation.



Figure 15. Effective reaction velocity, conversion and ferric sulphate ratio of multiple application of goethite Bayoxide E F 20; reaction temperature: 600 °C, feed gas composition: 10 vol.% SO₂, 18 vol.% O₂ and 72 vol.% N₂.

Conclusions

Sulphur dioxide oxidation experiments with ferric oxides were conducted at temperatures in the range of 450 - 650 °C and 5 - 28.5 vol.% SO2 applying ferric oxide microparticles as well as nanoparticles. Best yields were obtained at 600 - 650 °C with most pronounced differences in catalytic activity at 600 °C. Thermodynamic equilibrium was reached with hematite microparticles only in the case of 5 vol.% SO2 at 650 °C $(71.4 \pm 4.6 \%)$. Experiments with various ferric oxides were conducted with 10 vol.% SO2 at 600 °C showing that sulphur dioxide conversion rates in the range of 13.6 \pm 2.1 to 72.8 \pm 1.0 % are achievable without optimisation of the applied catalyst. The thermodynamic equilibrium (79.3 %), which is typically established, when vanadium pentoxide catalysts are used, was reached under neither of the tested conditions. Highest sulphur dioxide conversion was obtained with goethite material Bayoxide E F 20, while above-average catalytic activity was found for schwertmannite. Precipitation conditions did not significantly affect catalytic activity of ferrihydrite and schwertmannite, while preceding ageing in mother liquor promoted catalysis. Experiments with hematite and maghemite demonstrated that the catalytic activity depends on particle size as well.

Analyses of spent catalysts showed that in the course of catalytic reaction all catalysts were transformed into hematite. Additionally, the materials took up sulphate while specific surface area got lost. Insufficient sulphation during application caused low conversion rates, which was especially found for materials treated at high temperatures, e.g. 900 °C, before application.

In summary, these results are very promising. They show that it is possible to develop a ferric oxide catalyst bearing the potential of competing with vanadium pentoxide. However, conversion rate as well as long-term stability still have to be improved. Experimental results of this study as well as former investigations ^[6,16] show promising strategies to meet these challenges.

Experimental Section

Materials

Ferric oxide (<5 μ m) was purchased from Sigma-Aldrich Chemie GmbH, Munich, Germany, and maghemite (7 – 10 nm; 20 – 40 nm) and hematite (100 nm) where obtained from IoLiTec Ionic Liquids Technologies GmbH, Heilbronn, Germany. Bayferrox 110 (hematite), Bayferrox 180 (hematite), Bayferrox 415 (goethite), Bayoxide E III (hematite), Bayoxide E 8611 (magnetite) and Bayoxide E F 20 (goethite) were provided by Lanxess Deutschland GmbH, Germany. Aluminium oxide beads ProCerox Al 99 with a diameter of 1.0 – 1.4 mm were obtained from ProCeram GmbH, Willmenrod, Germany. Standards and all other chemicals were purchased from VWR International GmbH, Darmstadt, Germany, as well as Carl Roth GmbH & Co. KG, Karlsruhe, Germany. All chemicals had a minimum purity of >99 %, while ferric oxide content of examined pigments ranged from 95 to >99 %.

Helium, synthetic air (20 vol.% O_2 , 80 vol.% N_2) and nitrogen (5.0) were purchased from Praxair GmbH, Düsseldorf, Germany, sulphur dioxide (3.8) was obtained from Air Liquide Deutschland GmbH, Düsseldorf, Germany. Compressed air (oil-free, dew point 3 °C) was produced in-house.

Equipment

Mass-flow controllers (MFC) were the product of MKS Instruments Deutschland GmbH, Germany. IR-spectroscopy was done by using a Nicolet iS10 FT/IR spectrometer by Thermo Fisher Scientific Inc., Waltham, MA, USA. A gas flow cell equipped with silicon windows for IR measurements was produced by PIKE Technologies, Fitchburg, WI, USA. Heating regulation was done using a controller LR 316 by JUMO GmbH & Co. KG, Leipzig, Germany. X-Ray analyses were conducted with an X-ray diffractometer D5000 by Siemens AG, Munich, Germany. Physisorption experiments were done using an ASAP 2020 by Micromeritics GmbH, Aachen, Germany. Scanning electron microscopy (SEM) was performed on a JSM 7001F by Jeol Freising, Germany. Germanv GmbH. DTA/TG-MS/IR measurements were done on a STAR^e System by Mettler Toledo, Columbus, OH, USA, equipped with a quadrupole mass spectrometer (ThermoStar[™] by Pfeiffer Vacuum, Aßlar, Germany) and an IR spectrometer (Nicolet iS10 by Thermo Fisher Scientific Inc. Waltham, MA, USA).

Experimental setup

For detailed experimental conditions of ferric oxide precipitation the reader is kindly referred to [31]. All self-synthesized materials were annealed in a tube furnace for 8 hours at 300, 500 or 900 °C with overflowing compressed air at a volume flow rate of 10 L/h. Sulphur dioxide oxidation experiments were conducted using the experimental setup shown in Figure 16. It essentially consists of three Mass-Flo Controller (MFC) for gas dosing, a heated tube reactor and a FT/IR spectrometer equipped with a gas flow cell with silicon windows and an inner volume of 38.5 mL for continuous sulphur dioxide quantification. Wash bottles filled with concentrated sulphuric acid and 1 M sodium hydroxide solution were used for absorption of sulphur trioxide as well as sulphur

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dioxide. The reactor (inner diameter: 25 mm) was made from fused silica and was equipped with a glass drip as supporting surface for the catalyst layer. The latter consisted of a mixture of 10 g catalyst with 20 g aluminium oxide beads arranged between two layers of glass wool. The reactor was additionally equipped with a glass capillary reaching into the catalyst layer. This was used for measurement of reaction temperature with a thermocouple (type S) as well as regulation of heating. All connections were made of steel or PTFE/ETFE.



Figure 16. Experimental setup

Experimental procedure: While heating up to the reaction temperature, 200 sccm of synthetic air were led through the reactor and were afterwards diluted with 2 sLm compressed air. This mixture passed the FT/IR spectrometer for baseline measurement. After reaching the desired reaction temperature, the experiment started by adding sulphur dioxide (5.0 - 28.5 vol.%) to the synthetic air stream. Reactant concentration was adjusted by lowering volume flow rate of synthetic air to keep the volume flow rate through the reactor constant, so the oxygen concentration varied between 14.3 - 19.0 vol.%. Each experiment was carried out for 5 hours, after which heating was stopped and 200 sccm synthetic air were fed into the reactor for 1 hour, whereupon gas flow of synthetic air was shut down and compressed air flow rate was raised to 2.2 sLm for baseline measurement. Conversion rates were determined from remaining sulphur dioxide concentration in the exhaust gas during the last hour of operation, when catalytic reaction had reached a steady state.

Determination of sulphur dioxide conversion and sample characterisation

Sulphur dioxide conversion was measured continuously by FT/IR spectroscopy. For this purpose, extinction in the range of 1,362 to 1,363 cm⁻¹ was evaluated applying a resolution of 0.121 cm⁻¹. For studies on crystal structure of the product an X-ray diffractometer was used, which was equipped with a monochromator using Cu-K_a radiation and operated at 40 kV and 40 mA. Hematite crystallite sizes were calculated from half width of the hematite

peak at $2\theta = 33^{\circ}$ using the Scherrer equation (K = 0.89). Particle structure investigations were done by physisorption of N₂. Samples were prepared by outgassing at 90 °C for 6 h. Scanning electron microscopy (SEM) measurements were done at 3 and 5 kV. Samples were prepared on carbon tabs and metallized with gold. Sulphate content of the ferric oxides were estimated by analysis of mass loss during thermal decomposition. Therefore DTA/TG-MS/IR measurements were done. The temperature programme was: After holding the temperature for 10 min at 25 °C it was heated with 20 K/min to 400 °C. Then, temperature was increased with 10 K/min to 800 °C, which was hold for additional 30 min, followed by further heating up to 1,000 °C at a rate of 10 K/min.

Acknowledgements

Financial support by the German Research Foundation (DFG, grant number INST 267/125-1 FUGG) is gratefully acknowledged. The authors thank Lanxess Deutschland GmbH and ProCeram UG for supplying material samples. Regina Moßig is owed thanks for X-ray analyses and Anja Obst for SEM analyses.

Keywords: Sulphur dioxide • Ferric oxide • Nanoparticles • Catalytic oxidation • catalyst

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